CHAPTER 1: INTRODUCTION

1.1 BACKGROUND OF STUDY

1.1.1 Membrane Overview

In many industries and manufacturing plants, a variety of separation processes have been applied for separation of chemical components streams, purification of products or enhancement of process efficiency. Due to the huge choices available for separation processes, it is essential to take into considerations of different aspects when a separation process is required either technically and economically. Among those processes, membrane is one of the most commonly-used processes that can satisfy different objectives of the separation processes, ranging from concentration, purification, fractionation or reaction mediation.

Membrane can be described as "a selective barrier between two phases" (Mulder, 1996), whereby the feed stream will be divided into two streams, retentate and permeate streams. The product stream to be collect after the process bases on the objectives of the process as listed above. For instance, both streams can be collected for further purposes if purification is the main objective. Membrane can be either thick or thin, it can be synthesized or natural, charged or neutral. Mulder (1996) also mentioned that its working mechanism also depends on the morphology or structure of the membrane as figure 1.1 below:

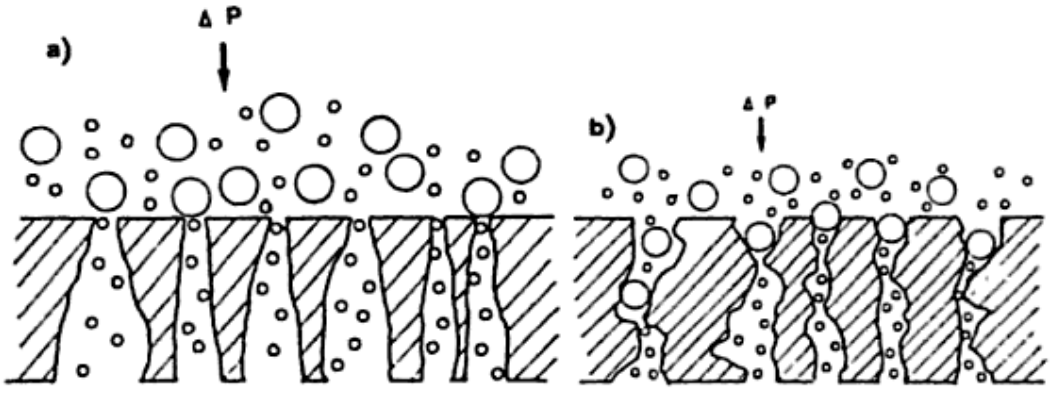
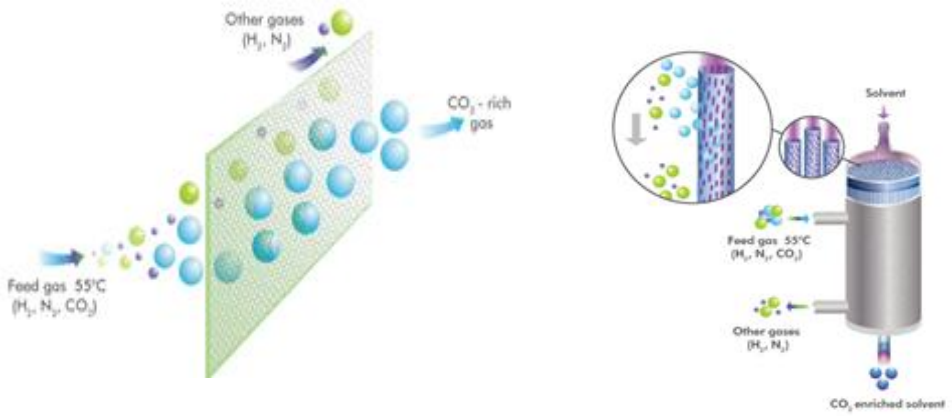


Figure 1.1 Morphology of membrane: (a) Symmetric – (b) Asymmetric
Source: *"Handbook of industrial membrane technology"* by Porter M. C. (1990)

Nowadays, membrane separation is one of the most popular separation techniques that are applied in many different industries as it can be synthesized from a large number of materials which made it applicable in the separation of many different components. It has also had some distinguished advantages compared to other separation processes that bring up the demand of membrane currently. Among those are the capacity for continuous separation, low energy consumption, the ease to be combined with other processes, no additives required and easy scale-up (Mulder, 1996).

According to Sutherland (2008), membrane can be generally categorized into two types which are flat sheet and tubular even though they can be shaped into other configurations afterwards, such as hollow fiber or spiral wound.

Figure 1.2 shows us the illustration of these two types in the industry.



(a) *(b)*

Figure 1.2 Membrane configurations: (a) Flat sheet membrane – (b) Tubular membrane
Source: *http://www.co2crc.com.au/research/demo_precomb_membrane.html*

Baker (2004) has also researched about membrane history and he showed that since its first studies in the eighteenth century, membrane technology has been continuously developing. Its first significant application can be mentioned as the testing of drinking water after World War II. Since then, a variety of membrane technology processes have been researched and commercialized. Typical applications of membrane are in the food industry, in medical processes such as artificially kidney or membranes for controlled drugs delivery systems. Nowadays, the processes of gaseous and liquid mixtures separation using membrane contribute to a great range of applications for membrane in

the market. For example, hydrogen separation and membrane for separation of nitrogen from air or carbon dioxide from natural gas are the most widely used processes of membranes by current technology.

Basically, membrane processes can be categorized into six different types (Baker, 2004). Reverse Osmosis (RO), Ultrafiltration (UF), Microfiltration (MF) and Electrodialysis (ED) are four developed processes that have many well-established unit operations while gas separation (GS) and pervaporation are developing processes whose market size and applications are expanding. In addition, there are also several other types of processes that are under research in order to solve their major problems before they can be commercialized in large scale plants. Typical new processes include carrier facilitated transports, membrane contactors, piezodialysis, etc.

As the number of applications in separation processes using membranes is increasing, the market for membrane is also increasing significantly. From Table 1.1, we can observe that the membrane demand in every region around the world increases gradually and they are expected to continuously increase in the next three years. The average demand of membrane worldwide grows around 9% while in Asia/Pacific, this number is relatively higher than the other regions which bring it from the second lowest demanding region to the highest in a few years time. With the high demand of membrane in Asia, it can be seen that the prospect of membrane technology in Malaysia is promising to be discussed for internal usage as well as for export purposes to other countries inside and outside Asia region

Table 1.1 World membrane market (2005-2015)

WORLD MEMBRANE DEMAND (Million dollars)					
Item	***2005***	***2010***	***2015***	***%Annual Growth***	
				2005-2010	***2010-2015***
World membrane demand	**8233**	**12550**	**19300**	**8.8**	**9.0**
North America	2741	4080	6070	8.3	8.3
Western Europe	2227	2670	3650	3.7	6.5
Asia/Pacific	2078	3645	6250	11.9	11.4
Other Regions	1187	2155	3330	12.7	9.1

Source: *Profile of international membrane industry market prospect (2008)*

1.1.2 Gas Separation Process

Among different types of membrane processes listed above, gas separation is the main process that will be used in this research. Baker wrote that the market for vapor separation systems is now at least $20-30 million per year with more than 100 large systems and at least 500 small systems have been installed and operated. The increase demand of gas separation membranes comes from the advantages of them over the other gas separation processes such as amine stripping plants, etc. Examples of the advantages can be the advantages of membranes such as low cost, low energy consumption. Moreover, gas separation membranes can provide simplicity for the process which is one of the most important factors in construction of a plant.

Currently, gas separation is used for many applications such as hydrogen separation, for example, hydrogen/nitrogen separation in ammonia plants, hydrogen/hydrocarbon separations in petrochemical applications, separating nitrogen from air, CO_2 and water removal from natural gas or organic vapor removal from air or nitrogen streams. Other applications of gas separation process can be seen in table 1.2.

For gas separation, membrane can be both porous and non-porous and the different in permeability of different components which passes through the membranes will determine the efficiency of the separation process.

Table 1.2 Gas separation applications

Common gas separation	Application
O_2/N_2	Oxygen enrichment, inert gas generation
H_2/Hydrocarbons	Refinery hydrogen recovery
H_2/N_2	Ammonia Purge gas
H_2/CO	Syngas ratio adjustment
CO_2/ Hydrocarbons	Acid gas treatment, landfill gas upgrading
H_2O/ Hydrocarbons	Natural gas dehydration
H_2S/ Hydrocarbons	Sour gas treating
He/ Hydrocarbons	Helium separation
He/N_2	Helium recovery
Hydrocarbons/Air	Hydrocarbons recovery, pollution control
H_2O/Air	Air dehumidification

Source: *"Application of membrane in gas separation processes: its suitability and mechanisms"* by Abedini R. and Nezhadmoghadam A. (2010)

1.1.3 Polyimide And Polyimide Membrane

Polyimides (PI) can be described as a class of thermally stable polymers based on stiff aromatic backbones. It is engineered for performance at very high temperature, in excess of 250^{o}C at a prolonged period of time. Therefore, it is very commonly used in aerospace, electronic and electrical industry where high temperature is required.

There are a variety of monomers as well as techniques available for the synthesis of polyimides. Laot (2001) introduced that the most widely used procedure is the two-step poly(amic acid) process where there is a reaction between a dianhydride and a diamine at ambient conditions in a dipolar aprotic solvent. This reaction bases on the nucleophilic attack of the amino group on the carbonyl carbon of the anhydride group. After the reaction, poly(amic acid) is formed which is subsequently cyclized into final polyimide. An example of the generalized mechanism of aromatic imide formation can be shown in Figure 1.2.

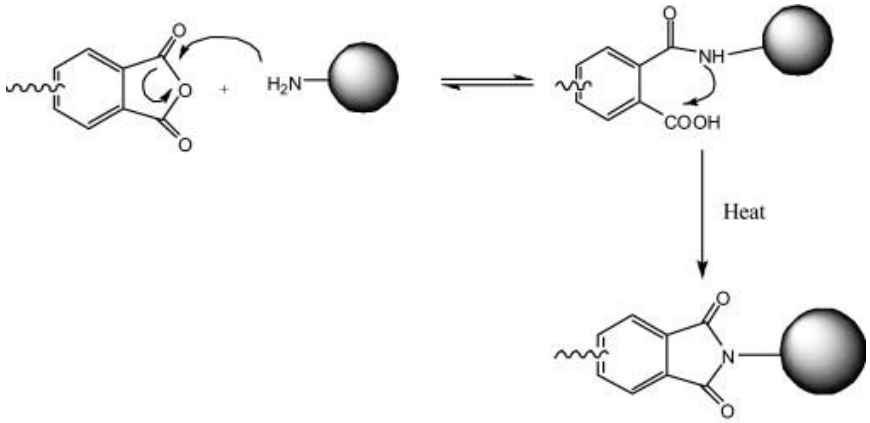


Figure 1.3 Generalized mechanism of aromatic imide formation

Source: *"New hydrogels based on symmetrical aromatic anhydrides: Synthesis, characterization and metal ion adsorption evaluation"* by Kavianinia I. et. al. (2012)

As we mentioned before, thanks to the various types of monomer available for its production, different types of polyimide are being manufactured in many different parts of the world. The consumption of PI is mostly centralized in Europe and United States region, as can be seen from Figure 1.4. However, for the Asian region, such as in India, China, Korea, Taiwan and Malaysia, the consumption of PI for different applications is also increasing at a relatively fast rate in the past few years. Therefore, it is promising that a focus on PI application can bring better outcomes in the near future.

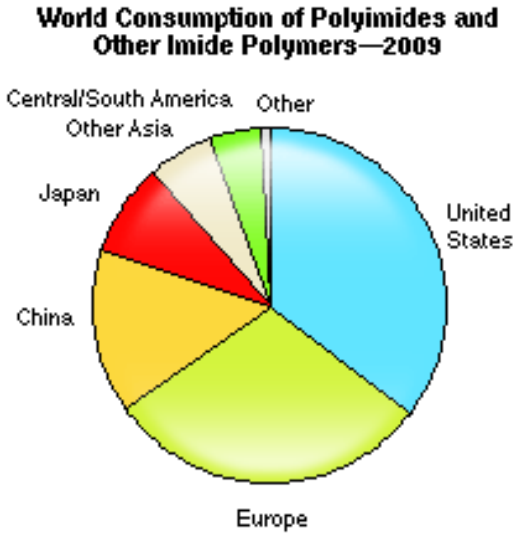


Figure 1.4 World consumption of PI in 2009

Source: *Profile of international membrane industry market prospect (2008)*

1.2 PROBLEM STATEMENT

1.2.1 Problem Identification

In this research, the focus is placed on the synthesis, characterization and optimization of polyimide membrane. Among the commonly polymer-based membranes that are used for carbon dioxide removal are cellulose acetate, polyimide, polyamide, polysulfone, polycarbonate and polyetherimide. Membrane from cellulose acetate is currently still the most widely used material. However, researches have addressed that polyimide provide certain advantages in the removal process of carbon dioxide thanks to its structure and characterization. Moreover, the market of polyimide is also increasing at a positive rate, especially in Asian region. Hence, it is decided that this research will focus on polyimide membrane. However, throughout the literature study, it was found that little emphasis was made in previous papers regarding the synthesis procedure of polyimide membrane and less focus on the optimization of these membranes for commercial purposes (Baker, 1999). Therefore this research will focus more on the synthesis steps of flat sheet polyimide using the dry-wet phase inversion method. In addition, more detailed work will be focused on the effects of variation of choices for membrane polymers, solvents, non-solvents and operating parameters on membrane morphology. Comparisons of these effects will be discussed through the characterization procedures of the synthesized membrane using several techniques available. Finally, the best parameters and

composition of this polyimide membrane will be optimized so that we can scale up to larger scope in the future.

It is also noted that membranes synthesized from this paper is mainly used for carbon dioxide removal application. We found that this removal necessary as carbon dioxide found in the natural gas stream is at a very high level of more than 80%. It can also combine with water which will form a highly corrosive mixture which will destroy the pipelines and equipments very rapidly. Moreover, it is a must to remove carbon dioxide in LNG plants in advanced to the final stage to prevent freezing in a low-temperature chiller. Testing of the effectiveness of the removal process can be compared to the current technologies used in the industry.

1.2.1 Significant of the project

According to the reasons stated above, this paper can be the pioneer to provide more detailed procedure of polyimide flat sheet membrane synthesis within the university scope. This can provide ease to following studies afterwards. Moreover, with the procedure that has been discussed for the synthesis process, it is also easier to modify the operating parameters as well as the membrane compositions to provide more knowledge on these effects on membranes. Moreover, as mentioned before about the growth of membrane technology in Asia/Pacific region as well as the gradual growth rate of gas separation processes, the employment of polyimide as a new material to replace cellulose acetate for carbon dioxide removal is getting more concern and it can bring unexpected effect that would make the removal process more efficient and effectively

1.3 OBJECTIVES AND SCOPE OF STUDY

1.3.1 Objectives

- To set up a manual experimental procedure for polyimide membrane casting.
- To study the effect of polymer concentration, coagulation bath composition and addition of binder on membrane's morphology.
- To characterize polyimide membranes by using FESEM, FTIR, TGA.

1.3.2 Scope Of Study

As the research consists of all the synthesis, characterization and optimization of the polyimide membrane, there are different approaches that have been used in each of the stage of the research.

- Synthesis:

In this research, it is decided that the synthesis of membrane will be based on dry-wet phase inversion method for a flat sheet membrane through manual casting.

- Composition of membrane: Variation of membrane composition based on selected 1 type of solvent, 2 types of non-solvents and binder addition.
- Parameters to study: Effects of polymer concentration, composition of coagulation bath and binder addition.

Observations and comparisons will be made on the membrane's morphology after synthesis process.

- Characterization:

A characteristics test is necessary to understand more about the morphology as well as membrane's component and pore's distribution. It was also required to check the availability of the lab equipments inside the university before we carry out these tests. Eventually, the analytical tests decided to study about the membrane characteristics are FESEM, FTIR, TGA.

1.4 RELEVANCY AND PROJECT FEASIBILITY

- Process Flow:

Table 1.3: Expected experimental process flow

No	Step	Duration
1	Experimental set-up preparation	30 minutes
2	Membrane solution preparation	18hours - 48 hours
3	Membrane casting	30 minutes
4	Solvent evaporation time	1 hour
5	Precipitation process	1 hour
6	Drying time	24 hour- 48 hours
TOTAL		**44 hours - 100 hours**

- Total Experiments: 15 (Can be done in parallel)
- Planned schedule and work allocation (Attached Gantt Chart)

As the project would be conducted within eight months of study, it is believed that this is a sufficient time for the completion of the project objectives as listed above. According to table 1.3, we have seen that parameters of membrane to be studied have been carefully chosen to suit the project timeline and in the same time, still demonstrate their great effect on performance of membrane. In addition, with a reasonable and detailed plan with specific time allocated for each part of the whole project as well as the preparation on project equipments and apparatus, we believe that the project can be completed during the time frame and can give good outcome by the end of its completion. Further study of the project to further states can also be recommended for better outcomes in the future.

CHAPTER 2: LITERATURE REVIEW

2.1 CONVENTIONAL CARBON DIOXIDE REMOVAL PROCESSES

As Stookey (2005) has stated in his research, the price of natural gases have been tripled since 2002 and therefore, it is essential to improve and ensure its quality before supplying for different purposes. One of the most serious concerns of the manufacturers is the removal of carbon dioxide (CO_2) from natural gas. There have been several treating techniques that have been used, for instance, amine treaters with the employment of typical amines as monoethanolamine (MEA), diglycolamine (DGA), etc. for the enhancement of this removal process, membranes have also been used in many plants to provide good pre-treatment of inlet gas and eliminate a high percentage of acidic gases like CO_2 from the process. Figure 2.1 shows the typical process of CO_2 removal from natural gas plant. Dortmundt (1999) has listed some common materials for CO_2 removal using in the industries such as polyamides, polysulfones, polycarbonates and especially the conventional polymer which is cellulose acetates (CA). However, recently in the industry, polyimide (PI) appear to be a more attractive type of material to new technology as it performs several advantages over cellulose acetates. According to Yampolskii (2010), the separation factors for CO_2/CH_4 are significantly higher using PI compared to CA for different gas inlet ranging from pure gas, mixed gas to other parameters variation such as temperature or pressure.

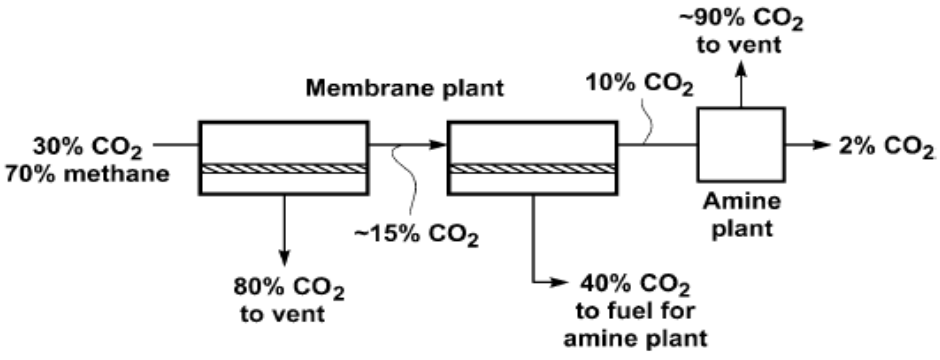


Figure 2.1 Typical membrane process for CO_2 removal in natural gas plant
Source: "Membrane technology and Applications" by Baker R.W *(2004)*

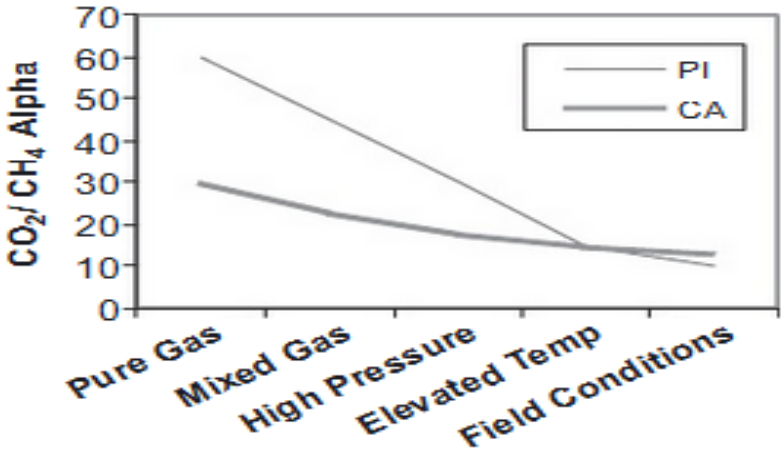


Figure 2.2 Separation factors for CO_2/CH_4 using PI and CA

Source: *"Basic Principles of Membrane Technology*" by Mulder M. (1996)

2.2 POLYIMIDE SYNTHESIS

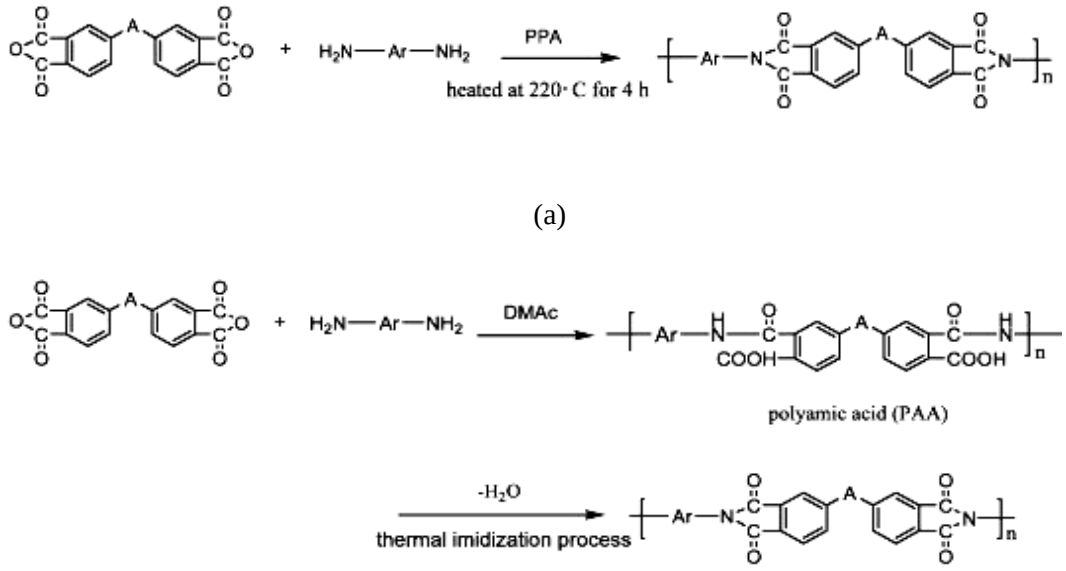
The synthesis process of polyimide is usually done through one out of these two schemes: one-pot synthesis and two-pot synthesis.

The conventional process is two-pot polymerization whereby a poly-amicacid will be formed first from the mixing of dianhydride and diamine in a polar aprotic solvent. Such solvents can be listed as N,N-dimethylacetamide (DMAc), N,N-dimethylformamide(DMF) or N-methyl-2-pyrrolidone (NMP). This poly-amicacid will be turned into polyimide afterwards using chemical or thermal cyclization reaction (Jin, 2009).

On the other hand, in one-pot polymerization is the direct route for synthesizing of polyimide. This process is used to solve such problems of two-step polymerization as the storage of poly amic acid or imidization process control. Vinogradova and Vigodskii et. al. established their first one-step route in 1970, followed by later improvements by other researchers. For this process, the direct polycyclization will be prepared from tetracarboxylic acid anhydrides with different diamines using nitrobenzene, ditolylmethane or sulfolane as solvents. In other researches carried out by Harris (1995), high boiling solvents are also used as solvents. However, they faced the issue of toxic carcinogen solvents. In another recent report by Wang et. al. (2008), one-step synthesis

of polyimide was introduced in the melt of salicylic acid, which allowed the synthesis of cyclized polyimides with high molecular weights.

Figure 2.3 shows the general process of polyimide synthesis using one-pot and two-pot polymerization.



(a)

(b)

Figure 2.3 Synthesis routes of polyimide

(a) One-pot synthesis – (b) Two-pot synthesis

Source: "*Homogenous one-pot synthesis of polyimides in polyphosphoric acid*" by Jin L. (2009)

2.3 PHASE INVERSION METHOD

2.3.1 Phase Inversion Method

Mulder (1996) has introduced carefully about the phase inversion method which is used in some membrane processes with lots of detailed information. Basically, phase inversion method is applied through several techniques: Solvent evaporation, controlled evaporation, thermal precipitation, precipitation from the vapor phase and immersion precipitation.

- Precipitation by solvent evaporation: The solution of polymer and solvent is cast on a suitable support. The evaporation of solvent will occur in inert atmosphere so that water will be excluded. Afterwards, a dense membrane will be formed.

- Precipitation from vapor phase: The mixture of solvent and polymer is exposed to a vapor atmosphere whereby the saturated non-solvent will exist in the same solvent. Due to the high concentration of solvent in the vapor phase, the evaporation of solvent from the polymer mixture will not occur. Instead, the non-solvent will diffuse into the membrane to form the porous membrane without top layer.
- Precipitation from immersion: In this case, the evaporation in air is introduced. If the solvent is miscible in water, the precipitation from the vapor will start here. The evaporation stage is often introduced by immersion precipitation exchange between solvent and non-solvent from the vapor phase leading to precipitation.
- Precipitation by controlled evaporation: In this case, the polymer will be introduced into a mixture of both solvent and non-solvent. Since the solvent is much more volatile compared to the non-solvent, it will be evaporated more during the evaporation step, leading to the higher concentration of non-solvent and polymer. Eventually, the polymer precipitation leading to a skinned membrane.
- Thermal precipitation: This method is used to prepared microfiltration membrane when the mixture of polymer and solvent is cooled until the evaporation of solvent occurs. This process also forms a skinned membrane as the previous case.

2.3.2 Flat Membrane Prepared by Phase Inversion

Using the phase inversion method, we can synthesize membranes either in flat sheet or in tubular form. From the objectives of the study, we emphasize on the flat membrane synthesis. The preparation of polymer consists of a few steps where by polymer is dissolved in solvent to form the polymer solution. It will then be cast upon a supporting layer and followed by the immersion into a coagulation bath where polymer precipitation occurs. Finally, the flat membrane will be sent for post treatments before it is sent for further study (Mulder, 1996).

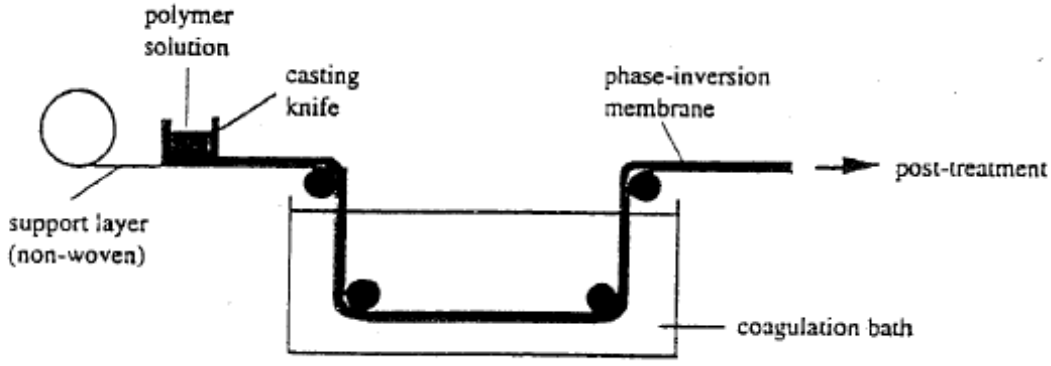


Figure 2.4 Schematic diagram of flat membrane synthesized by phase inversion method

Source: *"Basic Principles of Membrane Technology*" by Mulder M. (1996)

2.3.3 Dry-Wet Phase Separation Method

Normally, there will be several ways for the phase inversion process, including dry, wet or dry/wet phase separation. In this paper, we will use the dry-wet phase separation process in the synthesis of membrane as it is one of the most commonly used membrane process, together with thermally induced phase separation (TIPS), says Khulbe (2008). This technique was first established by Loeb and Sourirajan with the following steps:

- Preparation of polymer solution by mixing polymer and solvent with a specific polymer concentration.
- The viscosity bases on the molecular weight of the polymer, its concentration in the solution, the choice of solvent, etc.
- Cast the solution on a suitable surface to a pre-specified thickness.
- Allow partial evaporation of solvent, then immerse the casting solution into a non-solvent bath called coagulation bath.
- Precipitation process: Solvent and non-solvent exchange, evaporation of solvent. This leads to the solidification of polymer film.

  During the solvent evaporation, a thin skin layer of polymer is formed on the top of casting film. During the following exchange process, the non-solvent will diffuse into the solution through the thin solid layer while solvent diffuses out.

The composition change in the film is illustrated in figure 2.4 by the 3 lines (Line A, line B, line C).

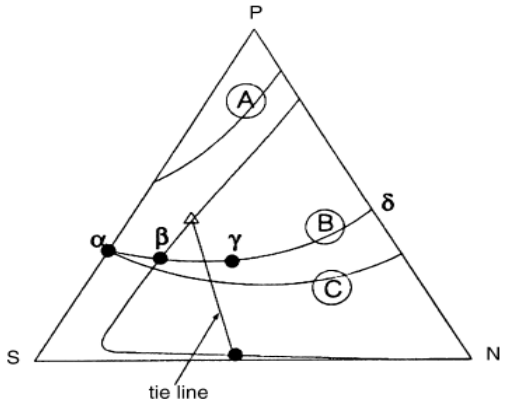


Figure 2.5 Triangular diagram of polymer (P),solvent (S), and nonsolvent (N).
Source: *"Synthetic Polymeric Membranes: Characterization by Atomic Force Microscopy"* by Khulbe et. al. (2008)

2.4 CHOICES OF POLYMERS, SOLVENTS AND NON-SOLVENTS

With the employment of PI as the original polymer for the synthesis of membrane for CO_2 removal, different research papers have been conducted using a variety of PI types. Zhang (1999) showed the different performance of membranes based on two different polymer types which are BPDA-ODA and BDA-ODA. The second type has demonstrated better selectivity after the process. Other polymers were also used in the following researches such as PMDA, BTDA in the paper of Niyogi for the preparation and characterization of polyimide membrane.

In addition, the difference in solvent choices also brings some effects to the membrane. Shao et. al. conducted some experiments for the synthesis of 6FDA/PMDA–TMMDA membrane using different solvents such as CH_2Cl_2, DMF and NMP (2004) . Results have shown that CH_2Cl_2 dissolves the co-polyimide at a relatively slower rate compared to the later two solvents. Based on the solubility parameter of these solvents, we can see the parameter of DMF is much closer to that of the co-polyimide compared to the other two. Therefore, it is more suitable to be chosen as the solvent for the process.

In other studies, it appears that the choice of non-solvent also plays an important part in the performance of polyimide membrane. Leblanc et. al. (2001) has shown the result in their study using different non-solvents for the mixture of solvent-polymer as DMF:

6FDA-mPDA that water appears to be a better non-solvent selection compared to alcohols since the compatibility of alcohols to 6FDA-mPDA is better than that of water. The results shows that a careful choice of non-solvent or mixture of non-solvent needs to be considered before the synthesis process takes place.

After the synthesis of membrane, mostly all of them will be sent for characteristic tests. The most common tests can be listed as SEM, FTIR, TGA and XRD. By performing these tests, the morphologies as well as the stability of these membranes can be analyzed. For instance, through the TGA test for the BTDA-ODA membrane synthesized in the experiment of Kim (2005) is very stable at high temperature and will only degrade at the temperature of 600-700^{o}C. This can ensure the membrane to enduce very high temperature processes.

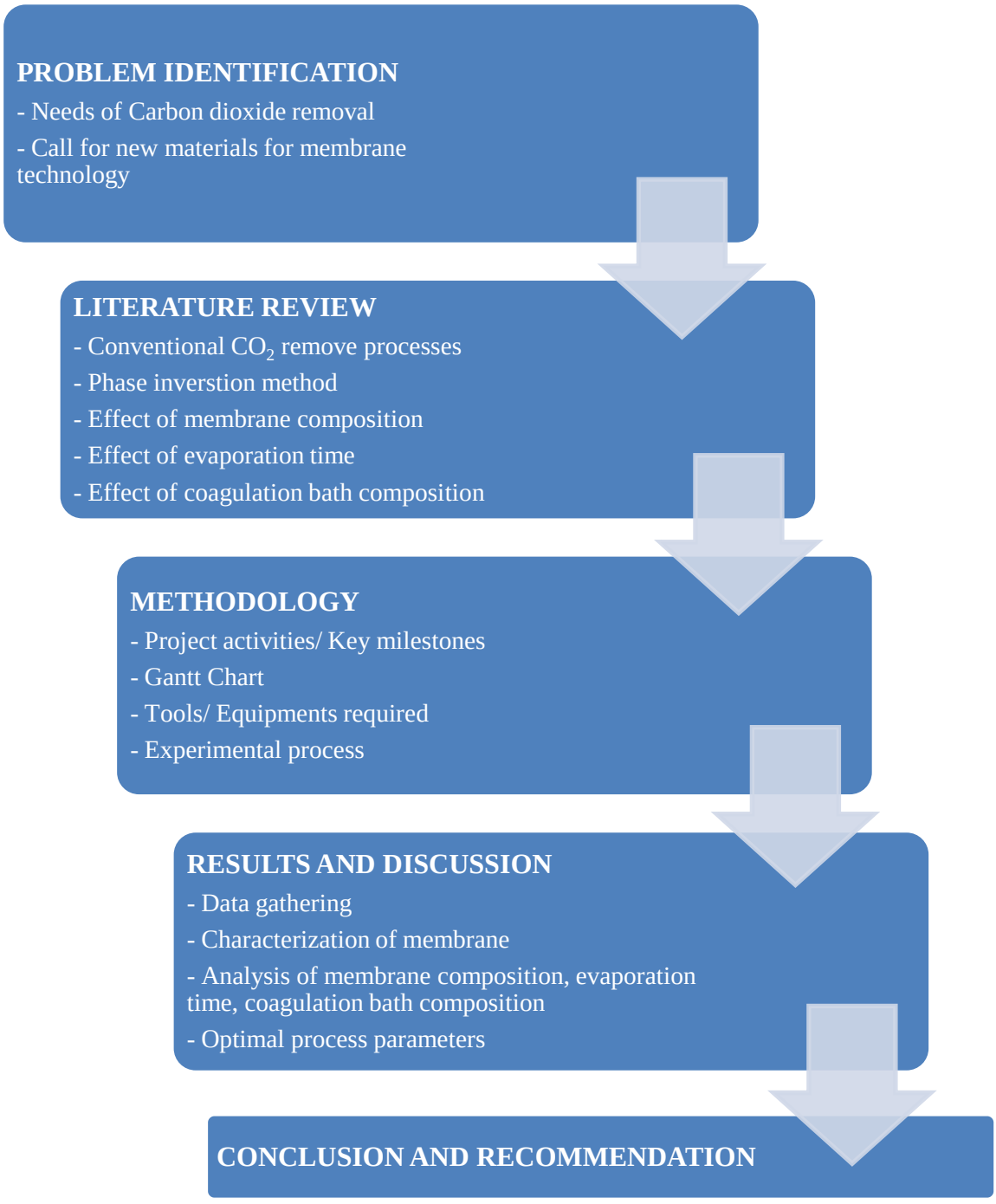
Besides the characteristics tests, different parameters have also been tested for each type of membrane such as the modifications in concentration, polymer type, coagulation bath composition, etc. In the book about the basic principles of membrane technology, there can also be a transformation from a porous to nonporous membrane just by adjusting the composition of the coagulation bath.

Choice of study:

Through the studies of previous papers, we decided to synthesize a flat membrane thanks to its simplicity in preparation which is suitable for laboratory scale. The solution will be casted on a supported non-woven polyester layer on top of a glass plate. We choose the mixture of BTDA/ODA as the original types of polymer for our experiment thanks to their popularity in membrane processes as well as its availability of supply from the commercial market. The chosen solvent is N,N-dimethylformamide (DMF) which can also be easily obtained from the laboratory and has proved to be a effective solvent in the synthesis of BTDA membranes. The coagulation bath will consists of both ethanol and water with specific ratio. With this specification, we will study the membrane characteristics through the tests listed above as well as the effect of significant parameters which are polymer concentration, coagulation bath composition and binder addition to the synthesis process.

CHAPTER 3: METHODOLOGY

3.1 PROJECT ACTIVITIES/ KEY MILESTONES



3.2 GANTT CHART FOR FYPII

Week Number	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
Activities/Milestone														
FYP II first briefing														
Meeting with Supervisor														
Lab space registration/ Apparatus collection														
Chemicals collections														
Equipments booking														
Experimental lab work														
Characterization of synthesized membrane														
Submission of progress reports														
Pre-sedex														
Draft of final dissertation														
Final presentation														
Dissertation submission														

3.3 TOOLS/ EQUIPMENTS REQUIRED

3.3.1 Chemicals/ Glasswares/ Equipments List

Table 3.1 Chemicals/ Glasswares/ Equipments List

Type	Number	Name	Amount	Supplier
CHEMICAL	1.	BTDA (3,3',4,4'-Benzophenonetetracarboxylic dianhydride)	100g	Sigma-Aldrich
	2.	BPDA (3,3',4,4'-Biphenyltetracarboxylic dianhydride	100g	Sigma-Aldrich
	3.	ODA (N-Oleoyl Dopamine)	100g	Merck
	4.	N,N-dimethylformamide (DMF)	2.5l	Merck
	5.	Ethanol	2.5l	Merck
	6.	DI water	2.5l	UTP
GLASSWARES & EQUIPMENT	7.	Mixing beaker	500ml	UTP
	8.	Mixing beaker	250ml	UTP
	9.	Two-neck round-bottom flask	50ml	UTP
	10.	Casting knife	300 µm	Plasmost Enterprise Sdn bhd
	11.	Glass plate	30 x 30 (cm^2)	-
	12.	Hot-plate stirrer		UTP
	13.	Coagulation bath		-
	14.	Micropipette		UTP
	15.	Stopwatch		UTP
	16.	Thickness gage		-
	17.	Dryer		UTP
	18.	Viscometer		UTP
	19.	FESEM (Carl Zeiss Leo Supra 50 VP)		UTP
	20.	FTIR (Perkin Elmer, System 2000)		UTP
	21.	TGA (Perkin Elmer)		UTP

3.3.2 Equipments

- **Field Emission Scanning Electrone Microscopy (FESEM):**

- ***Scope*:** FESEM is a type of microscopy that has a very high resolution which is obtained by the field emitter technology and the column with allows the resolution to reach an ultra-high resolution electron image at over x1000000. Therefore, very small micro-structural details of a sample can be obtained by using FESEM. With this performance, the equipment can be considered as the state-of-art electron microscope and it is currently applied in several fields such as nano-material research, electronics, new materials development, biology and genetics, etc.
- ***Significance:*** In membrane technology, FESEM is significantly effective as it can provide researchers with details about membrane particles shape and size given by its morphology. This is the first and foremost characterization test of a membrane after its synthesis to determine whether the membrane is symmetric or asymmetric, or to determine whether the pores are well distributed within the membrane.
- ***Principle:*** Under vacuum, electrons generated by a Field Emission Source are accelerated in a field gradient. The beam passes through Electromagnetic Lenses, focussing onto the specimen. As result of this bombardment different types of electrons are emitted from the specimen. A detector catches the secondary electrons and an image of the sample surface is constructed by comparing the intensity of these secondary electrons to the scanning primary electron beam. Finally the image is displayed on a monitor.
- ***Procedure:***
    - ✓ Set up operating conditions and check safety precautions
    - ✓ Turn on the online software for results display
    - ✓ Choose sample holder and mount sample with carbon tape, paint, or clips (carbontape is not suitable for non-conductive specimens. Carbon paint is best for conductivity, but requires several minutes to dry).

- ✓ Load the sample into the holder which may be available in different forms such as 6 and 4-inch wafers, wafer pieces, cross-sections, and mounting samples at pre-defined angles.
- ✓ Turn on the camera and start observing the image. Control the angle, resolutions, etc using the control panel.
- ✓ When the image is optimized, save the image with the suitable type of scans (line/frame average, line/frame integration, pixel average) and speeds.
- ✓ Carefully unload the sample from sample holder.

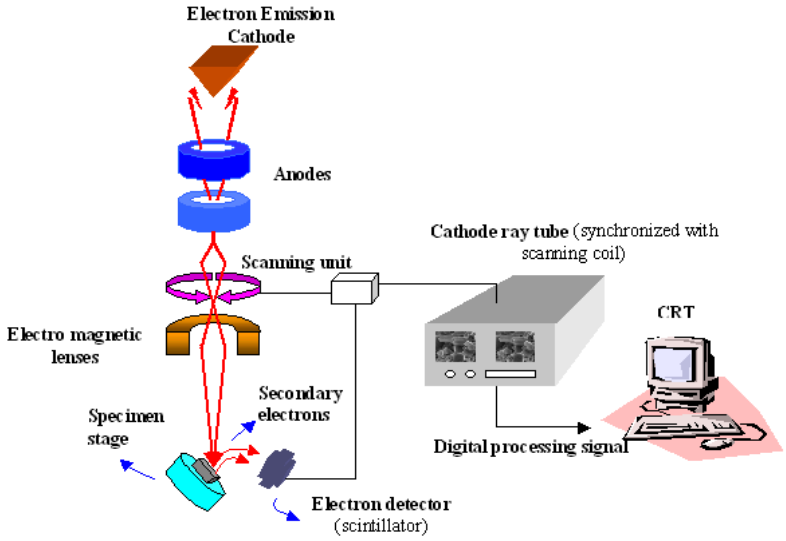


Figure 3.1 Working principle of FESEM

Source: *http://infohost.nmt.edu/~mtls/instruments/Fesem/FESEM%20principle.htm*

- **Fourier Transform Infrared Spectroscopy (FTIR):**

- ***Scope:*** IR spectroscopy is a chemical analytical technique which measures the infrared intensity versus wavelength (wavenumber) of light. The detected signals will be decoded by the mathematical technique called "Fourier Transform". By identifying the relationship between the intensity versus wavelength, we can determine the functional groups that exist in the sample analyzed.
- ***Significance:*** In membrane synthesis, it is essential to analyze the sample using FTIR as it can reflects the functional groups that exist inside the sample. With the information received, certain characteristics of the membrane can be

explained thanks to the chemical bonds and the individual characteristics of those bonds as well as from the interaction of various groups inside the sample.

- ***Principle:***
  - ✓ Infrared spectroscopy detects the vibration characteristics of chemical functional groups in the sample.
  - ✓ Infrared light interacts with the matter, chemical bonds will stretch, contract and bend.
  - ✓ Chemical functional group tends to adsorb infrared radiation in a specific wavelength range regardless of the structure of the rest of the molecule.
  - ✓ Correlation of band wavenumber position with chemical structure is used to identify a functional group in a sample.
  - ✓ No affected by temperature, pressure, sampling or change in molecule structure in other parts of the molecules
  - ✓ Specific functional groups can be monitored by infrared band (group wavenumbers)
  - ✓ Certain molecular vibration modes can be listed as Symmetric stretch, Asymmetric stretch, Scissor bending, Rocking bending, Twisting bending and Wagging bending.

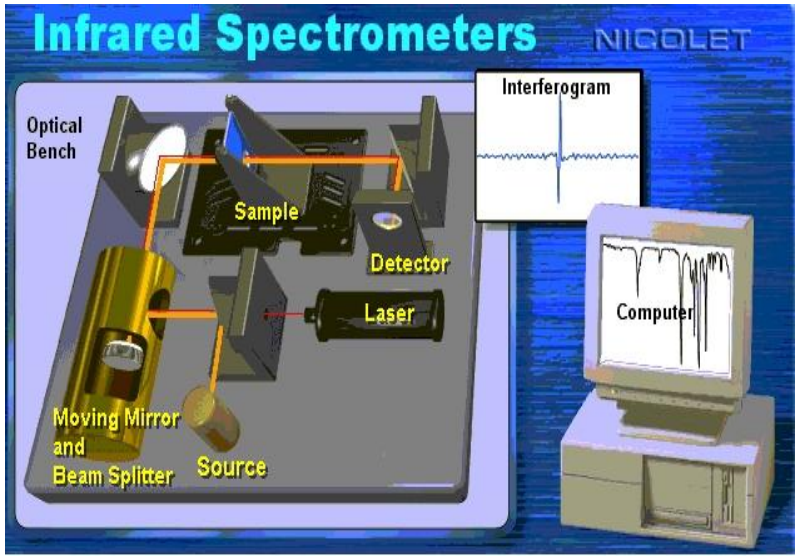


Figure 3.2 Working principle of FTIR

Source:*http://www.thermoscientific.com/ecomm/servlet/productsdetail_11152_L10693_82243_11961710*

- ***Procedure:***
    - ✓ Set up the operating conditions
    - ✓ Turn on the software and set up number of scans, resolution, apodizaiton, zero filling, final format, etc.
    - ✓ Run background samples and ensure the humidity is low.
    - ✓ Load the sample into the holder in the IR and run the analysis.
    - ✓ Optimize the final spectra by baseline correction and sample smoothing.
    - ✓ Labels all the peaks and eliminate unimportant peaks.
    - ✓ Save the final spectra, unload the sample and turn off the software.

- **Thermal Gravimetric Analysis (TGA):**

- ***Scope:*** The TGA provides a graph of mass loss versus temperature over the range of 25 to 1200 C. This analytical technique is widely used in polymer science, inorganic chemistry, fuel science, and geology. The experiments are usually run with a temperature ramp and can be carried out in inert atmospheres, such as nitrogen, to study thermal stability or volatility, or in oxidizing atmospheres to study oxidative decomposition. The mass losses can be characteristic of a material and, where the losses are in discrete steps, the TGA experiment can offer quantitative data on the course of decomposition.
- ***Significance***: TGA can be used in different applications which can help us determine several aspects such as composition of multi-component systems, thermal stability of materials, oxidative stability of materials, decomposition kinetics of materials, the effect of reactive or corrosive atmospheres on materials or moisture and volatiles content of materials**.**
- ***Principle:*** The sample container consists of a small platinum crucible suspended from the arm of a microbalance and situated in a small oven, the temperature of which is carefully monitored by a highly accurate thermocouple or some other appropriate temperature measuring sensor. The oven can be evacuated so the sample can heated and weighed in a vacuum (this can also improve thermal stability) and all volatile substances that are evolved are rapidly removed. Alternatively the atmosphere can be made inert by the introduction of a rare gas such as helium or argon, can be made oxidizing by the introduction of oxygen

or reducing by the introduction of hydrogen. In the more sophisticated and expensive instruments, the products evolved from the crucible can also be led into a capillary gas chromatograph, or a mass spectrometer (or a tandem instrument containing both) to help identify the products being generated. The sample can also be examined at elevated pressures if required.

- ***Procedure:***
  - ✓ Set up operating conditions.
  - ✓ Turn on software for results analysis.
  - ✓ Set up temperature range, operating atmosphere, inert rate, etc.
  - ✓ Load sample into a crucible hold as the sample holder and start analysis.
  - ✓ Monitor the output display and obtain the final TGA graph of the sample.
  - ✓ Save the TGA graph, unload the crucible and turn off the software.

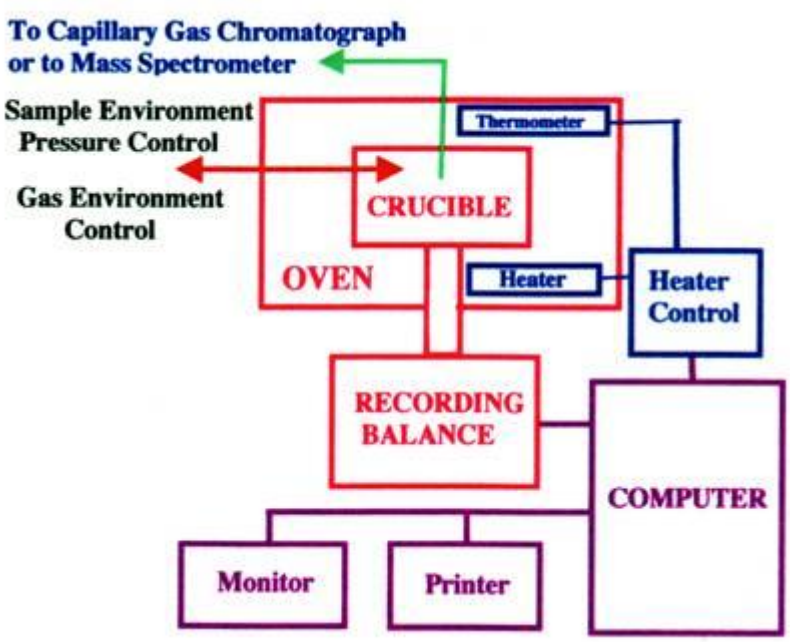


Figure 3.3 Working principle of TGA

Source:*http://physicalchemistryresources.com/Book5_sections/TA_Thermogravimetric%20AnalysisHTML_1.htm*

3.4 RESEARCH METHODOLOGY

As the research consists of all the synthesis, characterization and optimization of the polyimide membrane, the flow chart below can show the experimental flow of the study. Moreover, after the literature review, we have decided on the process parameters listed as below:

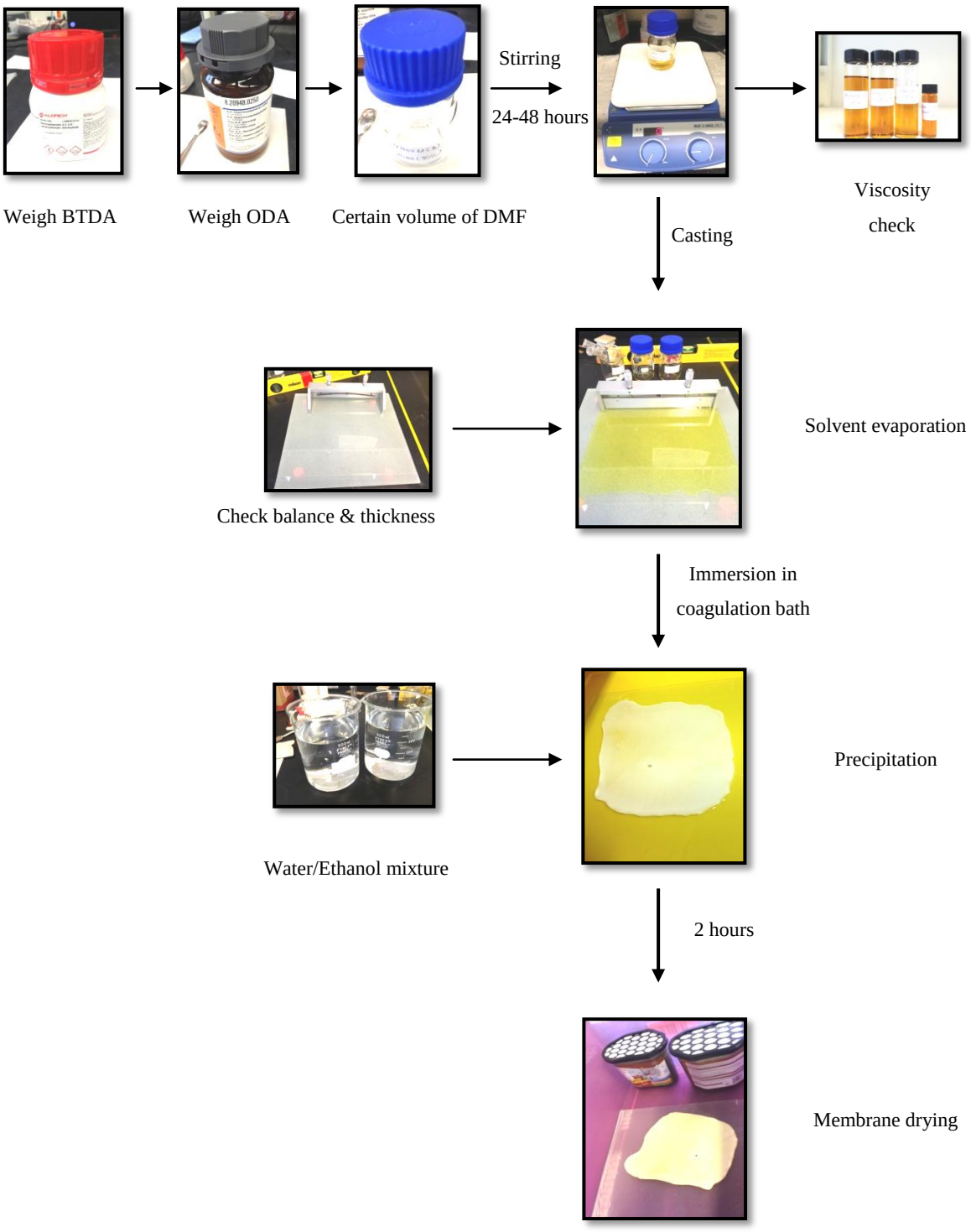
- ✓ Laboratory scope: manually synthesized and casted
- ✓ Focus:

Chemicals type	Polymer concentration	Binder Addition	Evaporation time	Coagulation bath composition (Volume)	Drying Time
BTDA/ODA/DMF	17wt%	0 wt%	1 hour	Water : Ethanol (7:3)	48 hours
	19wt%	1 wt%		De-ionized water	
	21wt%	3 wt%		Water: Ethanol (1:1)	

- ✓ Characterization tests: FESEM, FTIR, TGA, XRD

3.5 EXPERIMENTAL PROCESS

3.5.1 Experimental procedure



3.5.2 Chemicals

The monomers for membrane sysnthesis are prepared as followed: BTDA(3,3',4,4'-Benzophenonetetracarboxylic dianhydride) with 96% purity was bought from Sigma-Aldrich as well as BPDA (3,3',4,4'-Biphenyltetracarboxylic dianhydride) – 96%. Meanwhile, ODA (N-Oleoyl Dopamine) 99% was bought from Merck together with solvent DMF (N,N-dimethylformamide). Ethanol 99% and de-ionized water were provided by the university laboratory. The initial chemicals were employed in the synthesis process without any further purification.

3.5.3 Polymerization

As the feed chemicals are dianhydride and diamine, the polymerization step were required to obtain polyimide solution. The chemical process is explained as figure 3.5 below:

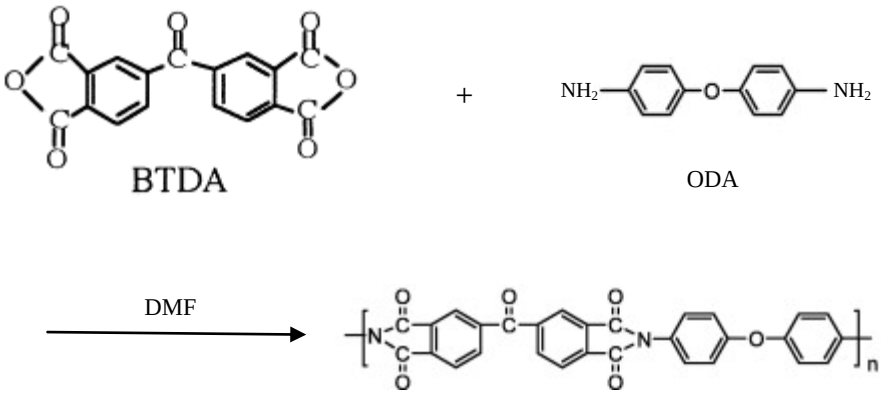


Figure 3.5 Mechanism of polyimide formation

A molar equivalent amount of BTDA and ODA was prepared by the beginning of the process. These two components were then mixed with a certain volume of DMF. The final concentration of BTDA/ODA in the solution was varied from 17wt% to 21wt%. The solution was then left for magnetic stirring without applying heat for 24 hours to 48 hours to form polyamic-acid. The final solution is observed to be a yellowish and viscous. The solution as then sent for viscosity check to ensure the sufficient viscosity for membrane casting.

3.5.4 Membrane preparation and characterization

The polyamic-acid solution is then prepared for casting after passing through a filter to eliminate large contaminant and un-dissolved components. The casting plate was prepared at the pre-specified thickness of 350μm. After balance checking, the solution was casted onto a glass surface and then left for partial solvent evaporation. After 1 hour, the glass plate was immersed in a coagulation bath that was filled with water and ethanol at a specific ratio. The solvent precipitation process was then left for 1 day before the membrane was removed for drying in a dehumidified container. The final membrane after drying was sent for further drying in the oven or for characterization tests.

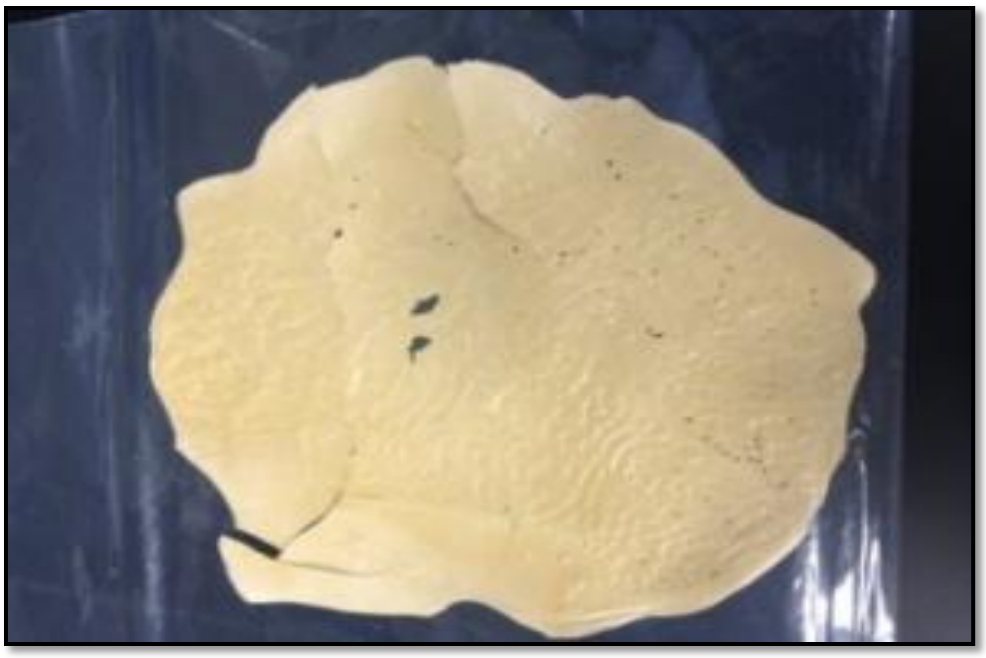
Characterization tests for this membrane are FESEM, FTIR, TGA.

CHAPTER 4: RESULTS AND DISCUSSIONS

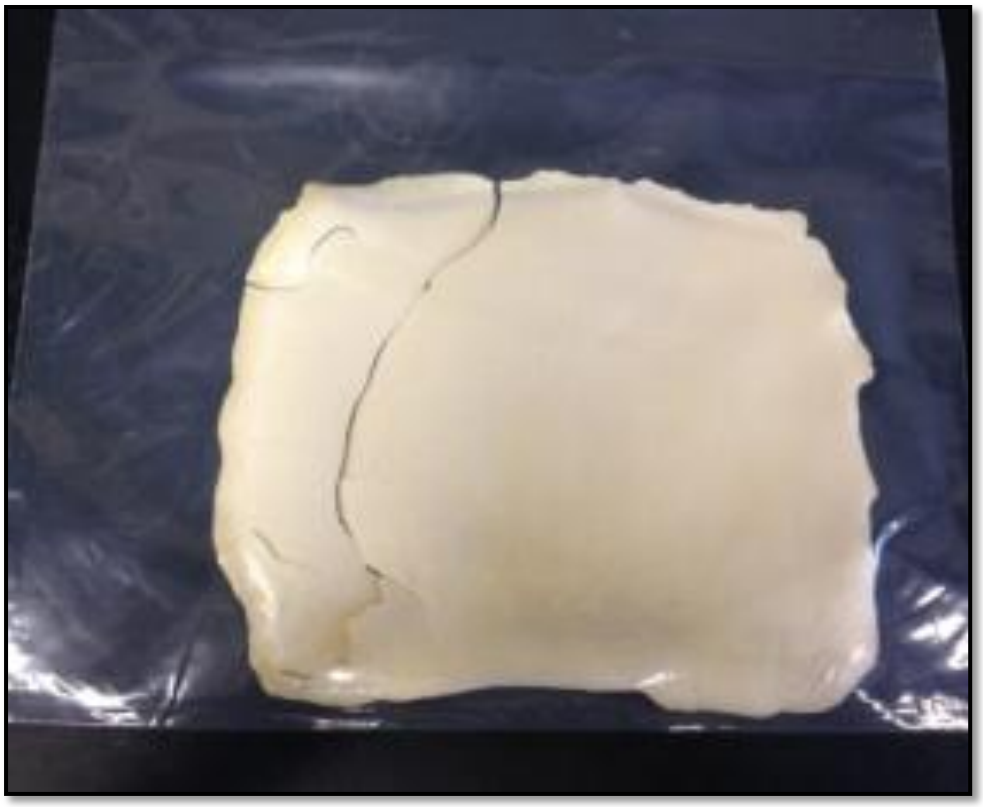
4.1 SYNTHESIS OF MEMBRANE

(a)

(b)



(c)



(d)

Figure 4.1: Synthesized membrane

(a) Cracked membrane

(b) Partially cracked membrane

(c) Membrane without binder addition

(d) Membrane with binder addition

In the first objective of the project which is to synthesize polyimide membrane from BTDA and ODA in the solvent DMF, several attempts have been made and improvements have been made for each case so as to obtain the most optimum operating parameters depending on the factors studied. Shortly, the membranes synthesized can fall under one of these 4 types as shown in figure 4.1

(a) Cracked membrane

Cracked membranes are usually obtained either during the stages where the evaporation of solvent takes place or when membranes are left for precipitation in non-solvent bath. In the first case, right after the membrane layer is left for partial evaporation of solvent, small cracks over the surfaces starts to appear. This can be explained as the solution is not viscous enough to stay over the surface and it tends to spread to different dimensions, causing the membrane to crack. In the second case, an unsuitable type of non-solvent bath can cause the layer to crack as it enters the bath. This can be explained as the high rate of de-mixing of solvent in non-solvent, typically in water: ethanol bath with 7:3 volume ratio. This prevents the precipitation process to be settled steadily. Lastly, membrane cracking can also occur during drying process. As the evaporation time is specified and kept as constant in all the experiments, the changes in different parameters can result in the existence of remaining solvent in the membrane when it starts to be sent for drying. Remaining solvent with high volatility can lead to the cracking of membrane in drying at higher temperature.

(b) Partially cracked brittle membrane

In some cases, with the suitable concentration of polymer in the poly amic acid solution, a nice layer of membrane is formed during the casting process. However, as it is immersed into the coagulation bath, as explained before, the high settling rate of solvent in non-solvent can crack the membrane layer. In this case, less cracking has

been observed as the ratio of non-solvents has been varied, which will be explained further in the later discussion part.

(c) Membrane without binder addition

As the observations have been made for the first two types of membrane, I manage to determine the suitable concentration of polymer in poly amid acid solution together with the composition of coagulation bath. Eventually, a fine membrane was produced after a long process as can be shown in figure 4.1 (c). However, it is also observed that this membrane layer is brittle and further enhancement should be made. Therefore, binder addition is employed in the later experiments.

(d) Membrane with binder addition

With the addition of glycerol as a membrane binder, keeping all other parameters at the optimum values as determined, a nice membrane layer has been obtained. Observations have shown that this layer is more elastic and less cracking is likely to occur. This positive effect of membrane binder will be explained in the later part.

4.2 EFFECTS OF POLYMER COMPOSITION

4.2.1 Polyamic-acid solution Viscosity

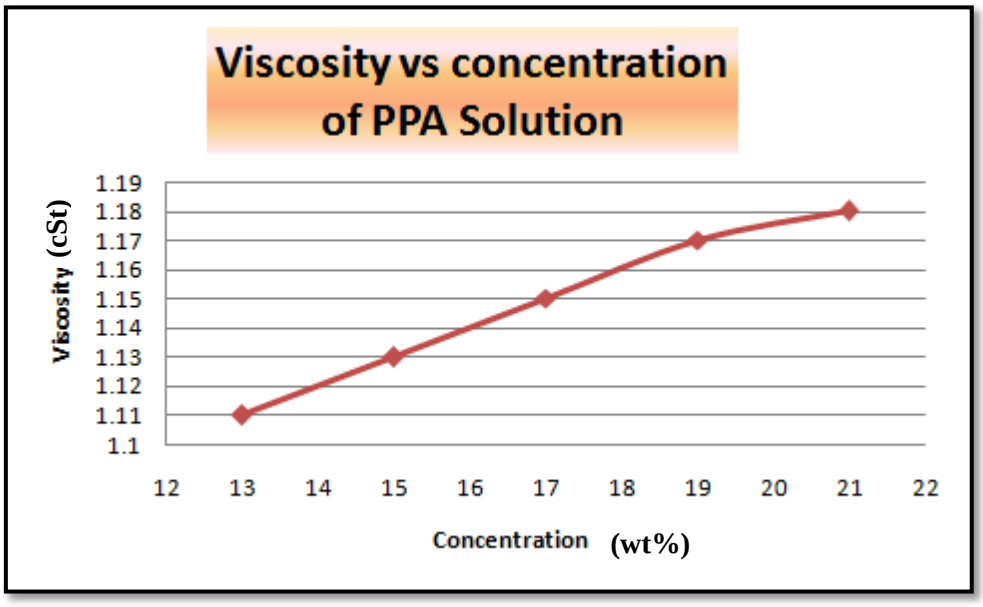


Figure 4.2 Graph of viscosity vs concentration of PPA solution

According to previous papers, calculations have been made so that the weight concentrations of dianhydrides and diamine in poly amicacid solution are varied from 13% to 21%. After the stirring process, these solutions were sent to a viscometer to determine their viscosity. This is an important step as it will determine the range of viscosity for solutions that are viscous enough to perform the casting process.

After testing, the viscosity was determined as shown in figure 4.2. It ranges from 1.11 to 1.18cSt. By observation, it is determined that the suitable range for viscosity of polyamic-acid solution was 1.15-1.18 which corresponded to the concentration of 17% to 21%. These values provide a viscous solution that can be used for casting and the solutions are not too viscous that may require degassing before casting. Below 17% of polymer weight in the solution, the solution becomes too dilute and is not suitable for further casting. The final chosen range also corresponds to the values obtained in a paper by Rozhanskii (2000).

Therefore, the final concentrations for polymer preparation process were decided as 17%, 19% and 21%.

4.2.2 Effects of polymer concentrations

As specified above, in the research, three values of polymer concentrations were chosen which are 17%, 19% and 21%. For each value of composition, same non-solvents have been employed for the precipitation process as well as same evaporation time and drying time.

It is observed that during the evaporation process, solutions with 17% of polymer concentration tend to spread in a certain range over the glass plate. This can lead to the less accuracy in membrane thickness as the layer will not be kept at 150μm as pre-determined. Moreover, it can also cause a too rapid evaporation of solvent from membrane layer that can finally crack the membrane which can be shown in figure 4.1 (a).

On the other hand, the solutions with 21% of polymer concentration tend to prevent the evaporation of solvent from membrane layer. A high concentration of solvent left after the evaporation process can be observed as the layer is sent for the next step of precipitation in coagulation bath. The top part of the layer still stays viscous and is spread widely in the bath as it is in contact with the non-solvent. This is also the reason for a membrane without a nice surface afterwards.

In conclusion, membranes with 19% of polymer demonstrates its effect as the best concentration as it is viscous enough to allow good evaporation and precipitation rates to produce membranes with nice surface in a suitable non-solvent composition.

Therefore, the optimum polymer concentration for membrane synthesis is **19wt%**.

4.3 EFFECTS OF COAGULATION BATH COMPOSITION

4.1.2 Design of experiments

Table 4.1: Experiments for different non-solvent types

Experiment number	Composition (BTDA-ODA/DMF)	Non-solvent (vol%	Binder addition (Glycerol) (wt%)
1	17%	Water : Ethanol (7:3)	-
2	17%	Water (100%)	-
3	17%	Water : Ethanol (1:1)	-
4	19%	Water : Ethanol (7:3)	-
5	19%	Water (100%)	-
6	19%	Water : Ethanol (1:1)	-
7	21%	Water : Ethanol (7:3)	-
8	21%	Water (100%)	-
9	21%	Water : Ethanol (1:1)	-

4.2.2 Effects of coagulation bath composition

From table 4.1, considering all the experiments with different concentration polymers in different composition of coagulation bath, we have observed the effect of non-solvent bath on membrane morphology and the conclusion of effectiveness of different non-solvent types can be shown as followed:

Water/Ethanol (1:1) > Water/Ethanol (7:3)> Water (100%)

The observations can be corresponded to the illustration as shown in Figure 4.1 above. For the first case when pure de-ionized water was used as non-solvent, the surfaces of the membrane were totally cracked once it is immersed into the coagulation bath (Figure 4.1a). However, as we start to add in ethanol to the bath with different ratios to water, positive improvements have been observed (Figure 4.1b, c). An equivalent volume ratio between water and ethanol demonstrate the best membrane synthesis.

This can be explained as DMF has high affinity to water which leads to constant de-mixing of the solution right the moment the casting film is immersed in the non-solvent bath. This will finally cause the membrane to crack. With the addition amount of ethanol

in the non-solvent composition, the -OH group of ethanol helps to link monomers together besides its original effect which is to remove all the remaining solvent from the membrane layer.

Therefore, the most effective coagulation bath composition is **DI water: Ethanol (1:1 volume ratio)**

4.3 EFFECTS OF BINDER ADDITION

4.3.1 Design of experiments

Table 4.2: Experiments for binder additions

Experiment number	Composition (BTDA-ODA/DMF)	Non-solvent (%vol)	Binder addition (Glycerol)
10	17%	Water : Ethanol (1:1)	1%
11	17%	Water : Ethanol (1:1)	3%
12	19%	Water : Ethanol (1:1)	1%
13	19%	Water : Ethanol (1:1)	3%
14	21%	Water : Ethanol (1:1)	1%
15	21%	Water : Ethanol (1:1)	3%

4.3.2 Effects of binder addition

Due to the fact that polyimide membranes synthesized are brittle and can be cracked easily. It is necessary to enhance its elasticity so that it can undergo the separation process of carbon dioxide removal afterwards which may be carried out under a certain pressure. Therefore, binder is added into the membrane composition which has shown promising effects on membrane final condition. However, to maintain the structure of polyimide membrane, a very small amount of binder was added. In this case, glycerol was added into the process with either 1% or 3% of concentration. The consideration of glycerol in this research is explained by the effect of the –OH groups in glycerol. The three hydroxide groups play a role as binders and connect the unconnected monomers inside the solutions together, which finally forms a membrane without cracking. However, as both cases shows the quite similar effect, it is advised to add only 1% of

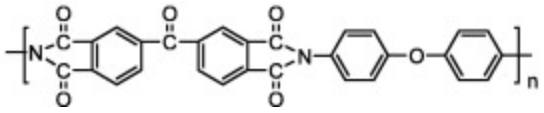
glycerol so that there would not be further changes in polyimide structures which can lead to unexpected effects or reactions.

Therefore, the suitable addition of binder is **glycerol (1wt%).**

4.5 CHARACTERIZATIONS

4.5.1 FTIR Analysis

We have known the structure of Polyimide as followed:



From the FTIR graph obtained by analysis, we can recognize the absorption band at several points shows the functional groups in the final polyimide membrane.

First of all, the sharp and strong absorption peak at 3398.74 cm^{-1} shows the the terminal alkyle group which exists in the amide structure. We also observed the benzene group at 1655cm^{-1} and the broad band from 2700-3100cm^{-1}. The absorption band from 1391 to 1543 cm^{-1} shows anhydride C=O group. Therefore, we can see that this analysis is corresponding to the structure of polyimide as we expected. A table of absorption ranges for different functional groups can also be found by the end of the report.

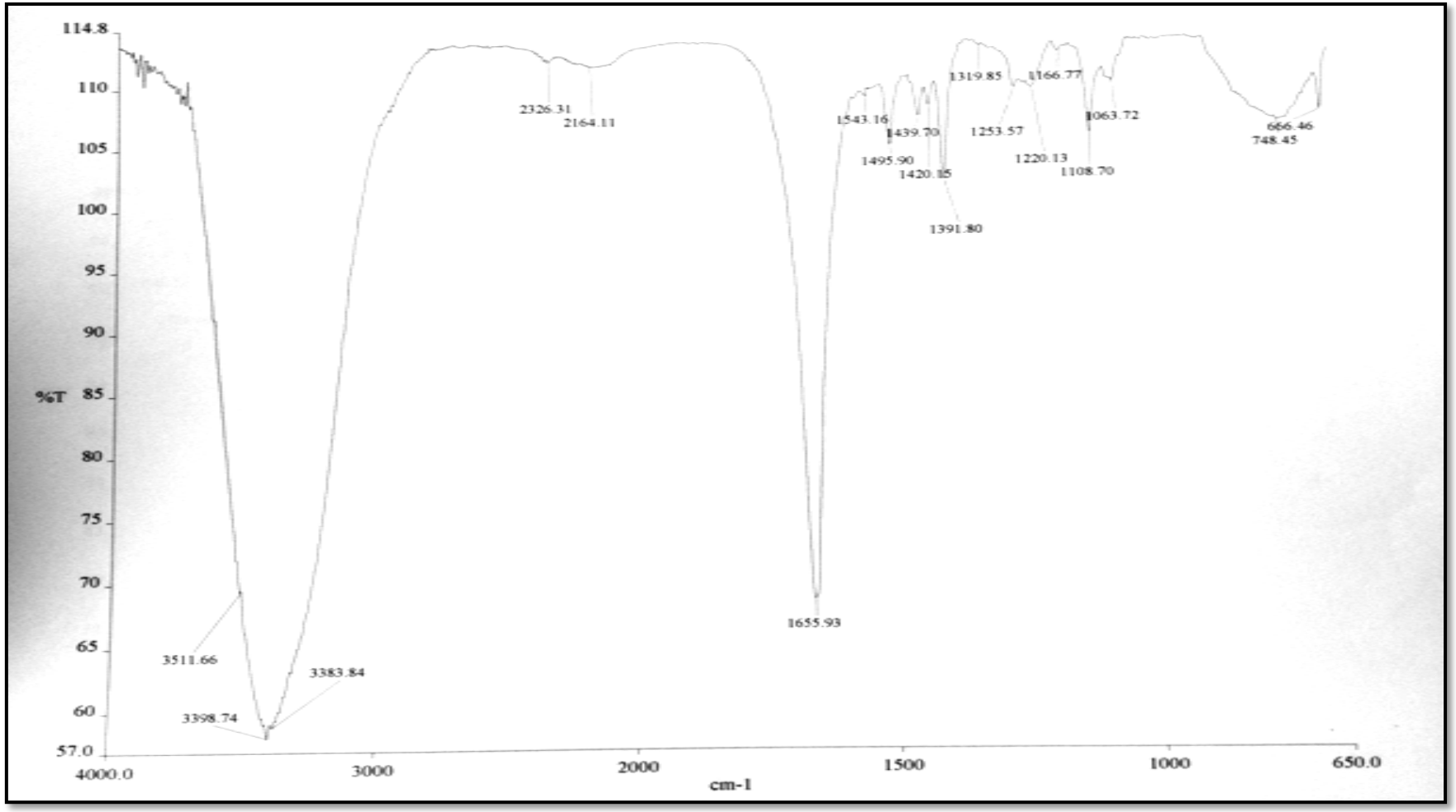


Figure 4.3: FTIR analysis graph

4.5.2 TGA Analysis

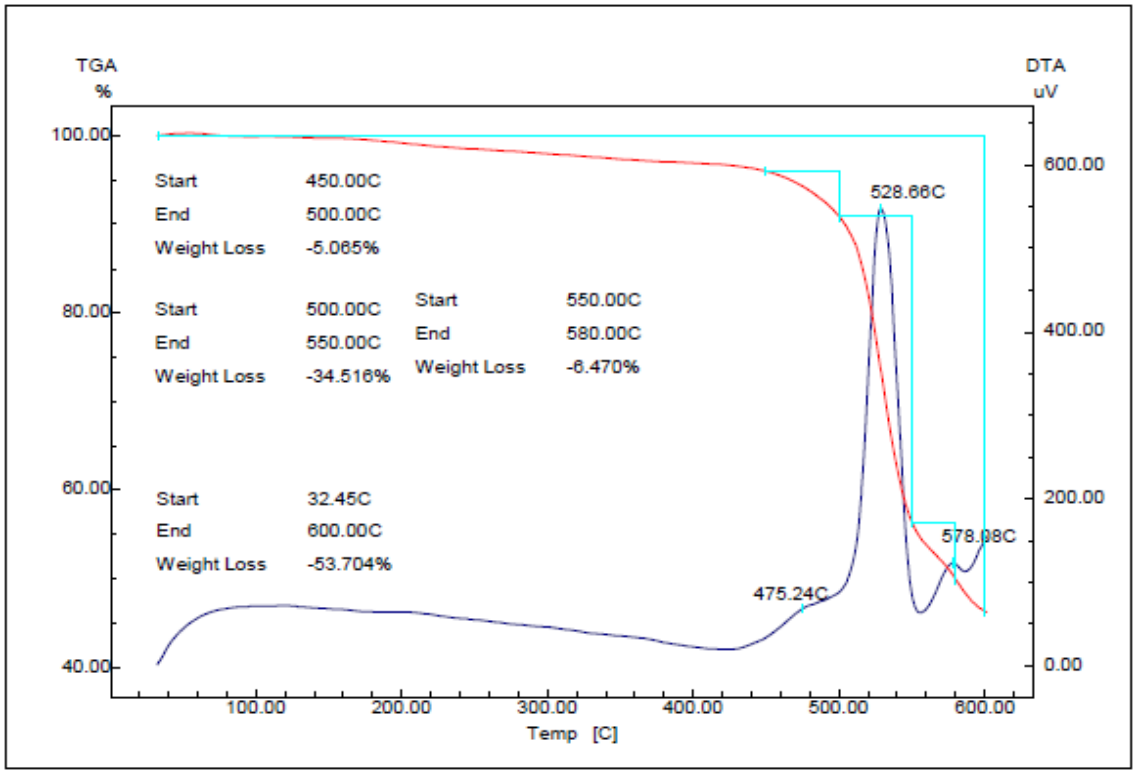


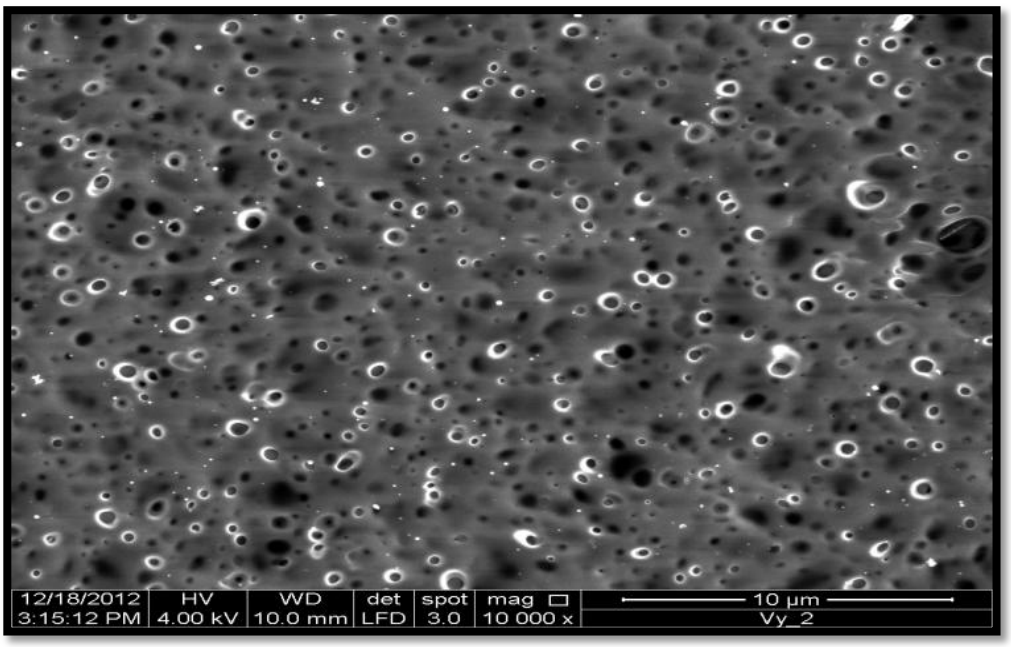
Figure 4.4: TGA analysis graph

Through this TGA analysis, we can determine the maximum mass loss is 53.704% when the temperature is raised to 600^{o}C. The maximum loss point at 561.49^{o}C for polyimide is observed. Therefore, we can see that our membrane can withstand relatively high temperature, which is suitable for processes which require high temperatures, compared to previous membrane materials such as polysulfone or cellulose acetate.

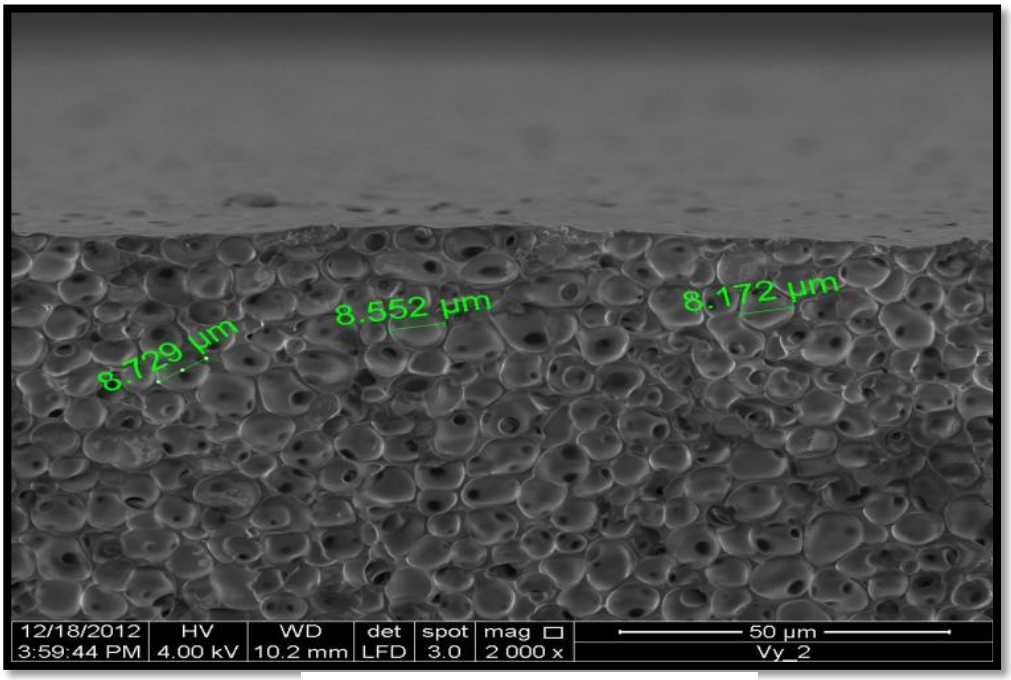
4.5.3 FESEM Analysis

Different magnifications of membranes were captured ranging from 3000x to 10000x. Surface images of membrane show that this type of membrane is a dense membrane. The surface is generally clean without contaminants. Small pores are observed on the surface.

Cross sectional images are also captured in this case. Under the thin layer surface, the lower part is porous. The typical diameter of pore is 8.5μm and the typical thickness of membrane is 350 μm as shown in the figures below.



(a)



(b)

Figure 4,5 FESEM images

(a) Surface – (b) Cross sessional

CHAPTER 5: CONCLUSION

From the research, we concluded that polyimide synthesized from BTDA/ODA monomer with DMF as the solvent has shown a promising outcome for polyimide synthesis. Several factors that have been studied in the research such as polymer concentration, coagulation bath composition and the binder additions have shown their effects on the membrane synthesized. After several experiments, the optimum polymer concentration is 19% with the non-coagulation bath consisting of water and ethanol at equal volume percentage. An addition of around 1% of glycerol is also encouraged to strengthen the condition of this membrane. Finally, the FTIR analysis has also shown the functional groups in these synthesized membranes which are corresponding to polyimide structure. These groups can be used to explain some characteristics of the membrane synthesis. TGA analysis has also been carried out and ensures that the synthesized membrane has high heat resistance and is suitable to be used for high temperature process. FESEM, in addition, has shown clearer images to the morphology of membrane after synthesis.

CHAPTER 6: RECOMMENDATIONS

For further extension of the project, further analysis for membrane characterizations using XRD is encouraged. In addition, further experimental work on other concentration/ compositions are encouraged. It is suggested that certain types of polyimide can be examined such as 3,3,4,4-Biphenyltetracarboxylic Dianhydride (BPDA) for effect comparison. A mixture of both dianhydrides is also suggested to maximize the effect. Other types of popular non-solvents are also suggested for further study such as methanol or acetone. Last but not least, performance testing of membrane on CO_2/CH_4 separation pilot should be done to conclude the project.

REFERENCES

Baker R.W. *"Membrane technology and Applications".* Johns Wiley and Sons Ltd. 2004

Baker R. W. *"Membranes for Vapor/Gas Separation".* Membrane Technology and Research, Inc.Dortmundt D. "*Recent Developments in CO_2 Removal Membrane* Technology". 1999

Gary D. Christian. "*Analytical Chemistry***",** 6th Ed., Wiley, QD101.2 C57 2003

Harris F.W., Cheng S.Z.D., *"Process for preparing aromatic polyimide fibers"*. US Patent 1995;5,378,420.

Hasanain F., Wang Z.Y. *"New one-step synthesis of polyimides in salicylic acid"*. Polymer, 49 (2008), page 831–835

Jin L., Zhang Q., Xu Y., Xia Q., Chan D., *"Homogenous one-pot synthesis of polyimides in polyphosphoric acid"*. European Polymer Journal, Volume 45, Issue 10, October 2009, Pages 2805–2811.

Kim Y. H., Park H. B., Lee Y. M. *"Preparation and characterization of carbon molecular sieve membranes derived from BTDA–ODA polyimide and their gas separation properties"*. Journal of Membrane Science 255 (2005) 265–273

Laot C. M., Dr. Ravi Saraf, Dr. Eva Marand, Dr. Garth L. Wilkes, Dr. Richey M. Davis, Dr. Herve Marand. *"Gas transport properties in polycarbonate - Influence of the cooling rate, physical aging, and orientation"* (2001).

Leblanc N., Le Cerf D. , Chappey C., Langevin D., Me´tayer M. , Muller G. *"Influence of solvent and non-solvent on polyimide asymmetric membranes formation in relation to gas permeation".* Separation and Purification Technology 22-23 (2001) 277–285

Mulder M., *"Basic Principles of Membrane Technology*". 1996

Niyogi S., Adhikari B. *"Preparation and characterization of a polyimide membrane"*. European Polymer Journal 38 (2002) 1237–1243

Shao L., Chunga T.S., Wensleyd G., Goh S.H., Pramodac K.P. *"Casting solvent effects on morphologies, gas transport properties of a novel 6FDA/PMDA–TMMDA copolyimide membrane and its derived carbon membranes"*. Journal of Membrane Science 244 (2004, p 77–87

Sutherland K. *"Profile of the international Membrane Industry Market Prospects to 2008".* Elseiver Advanced Technology. (2008)

Vinogradova S.V., Vygodskii Y. S., Korshak V.V., "*Features of polyimide synthesis by one-step high-temperature polycyclization"*. Vysokomolekulyarnye Soedineniya, Seriya A, 12 (9) (1970), page 1987–1993

Zhang J., Lu J., Liu W., Xue Q. *"Separation of CO_2 and CH_4 through two types of polyimide membrane"*. Thin Solid Films 340 (1999) 106±109